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(54) NEW DYEING PROCESS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a new dyeing process for the colouration of cellulose textile materials.

A number of physical forms of cellulose textile materials exist which are difficult to dye in level shades, owing to an apparent difficulty in having the dyestuff diffuse evenly throughout the material being dyed. Typical of such forms are materials comprising a plurality of layers of tightly woven fabric, packages of spun yarn, e.g. 3 cord mercerised sewing yarn, 7 cord mercerised embroidery yarn, heavy ducks, drills, webbing, belting, tapes with beaded edge, "ladder-web", and tapes with draw-strings for curtain attachment, filament viscose cakes and all dense packs of non-spun cellulose fibres.

It has now been found that such materials can be dyed to give well-penetrated level results by certain classes of reactive dyes by contacting the material in a neutral or slightly acid aqueous medium containing an electrolyte with the dyestuff at a temperature above 100°C for a sufficient period of time until the desired penetration and exhaustion are achieved, then fixing the dyestuff on the material by treatment of the coloured material with an acid-binding agent.

The essential novelty of the new process lies in the unexpected discovery that the majority of water-soluble reactive dyestuffs are almost as stable to hydrolysis in weakly acid or neutral aqueous dyebaths at temperatures of 100 to 140°C as they are at the lower temperature of 75 to 85°C which has hitherto been the maximum temperature recommended for their use in dyebaths, the only exception of notable importance being the class having a dichloro-*s*-triazine group as the cellulose-reactive group.

[*Price 25p*]

Reactive dyes which have been found to be effective in the new process include dyes containing di- and tri-chloropyrimidine, sulphatoethyl sulphone, sulphatoethylsulphonylamino, 5 - chloro - 6 - methyl - 2 - methylsulphonylpyrimid - 4 -yl, β - (4,5 - dichloropyridaz - 6 - on - 1 - yl)propionyl, acryloyl, β - phenylsulphonylpropionylamino, 2,4 - dichloropyrimid - 5 - yl, 2 - chlorobenzthiazol - 6 - yl, - 1,4 - dichlorophthalazin - 6 - yl, dichloroquinoxaline, β - chloroethylaminosulphonyl and, more especially mono - chloro - *s* - triazine groups containing amino, etherified hydroxy or anilino or substituted anilino groups. The dyes include members of the phthalocyanine, anthraquinone and azo, including monoazo, disazo and metal complex azo series.

In order to determine suitability for use in the new process, the following simple test has been devised:—

Two dyeings are carried out on cotton hanks using equal amounts of the dyestuff. In each case the dyebath contains also 80 g/l of common salt and 5 g/l of sodium - m - nitrobenzene sulphonate. (a) dying is carried out for 45 minutes at 120°C at pH 5.0—5.5 (0.15 g/l of acetic acid), then the liquor is cooled to 80°C, sodium carbonate is added (20 g/l) and dyeing continued for 45 minutes. (b) dyeing is carried out for 45 minutes at 80°C under neutral conditions, then sodium carbonate is added (20 g/l) and dyeing continued for 45 minutes. Both hanks are then rinsed in water and scoured at the boil in 0.3% detergent for 15 minutes to remove loose dyestuff.

In many cases it will be found that the two dyeings are of equal strength. Where however that produced by method (a) is weaker than that produced by method (b), the difference can be visually estimated using a geometric grey scale card as used for the effect of washing tests on dyeings, B.S.2663:1961. A dyestuff is considered suitable if the difference in depth is no greater than a grading of 4 on this card. However, a reactive dyestuff containing the dichloro- or dibromo - *s* -

triazine group is too unstable, even at 80°C, to be suitable for use in this new process.

The following cellulose-reactive dyestuffs, referred to by their Colour Index (Reactive) reference numbers have, for example, been found to pass this test:

Black 8
Brown 2, 7, 9, 17 and 19
Blue 2, 3, 5, 19, 21, 25, 26, 40, 46, 49, 53, 64 and 71
Green 5 and 8
Orange 2, 7, 12, 13, 23, 25, 32, 35 and 43
Red 3, 13, 19, 56 and 58
Yellow 3, 6, 15, 18 and 33.

The new process can be carried out in a variety of dyeing apparatus capable of dyeing at temperatures above 100°C, e.g. *Package-dyeing vessels* for cheeses, cones, cops, beams, torpedoes, hanks, packed warps, ribbons, tapes, narrow woven fabrics or all classes of piece goods wound on perforated holders, loose stock or fibre vessels, pressure jigs, winches and jet dyeing machines.

The new process can be conveniently put into practice by immersing the material to be dyed in the dye liquor which may be initially warm, e.g. about 40°C, then heating to dyeing temperature, preferably 120—125°C and maintaining at this temperature until the desired penetration and exhaustion have been achieved. Usually this will take from 30 minutes to 1 hour, but shorter or longer times may be advisable in special cases. Thereafter, in the preferred method of operating, the acid-binding agent used to fix the dyestuff on the fibre is added to the dye-liquor, preferably after cooling the latter to 80—90°C. Alternatively the material may be transferred to a separate vessel for treatment with a solution of acid-binding agent, or the dye-liquor may be drained off and replaced by a solution of acid-binding agent.

The dye-liquor can contain the usual additives, of which a neutral or weakly acid salt is essential, in general, to achieve adequate exhaustion. In this connection, there may be used sodium chloride or sodium sulphate at concentrations of 10 to 100 grams per litre, together if so desired with small amounts of acid salts e.g. sodium dihydrogen phosphate, to bring the pH of the dye-liquor within the range of 6.0 to 7.0. There may also be present other conventional additives, in particular it is desirable to have present a mild oxidising agent e.g. sodium nitrobenzene sulphonate.

The invention may be illustrated by the following Example in which parts are by weight:

Example

The material to be dyed consisted of a cotton tape about 1 3/8 inches wide, which had been folded around a piece of cord and centre-sewn. The cotton tape comprised:

		turns per inch
Tape	2 ply/18's cotton	20
Cord	4×4 ply	4.1
	4 ply	8.8
	Single/14's	28

i.e. a very hard, dense mass of cotton having a weight of 12.0 grams per linear yard, and had an intended use in the manufacture of zip fasteners.

When dyed in the usual manner at 80°C, it was found that penetration of dyestuff into the centre-sewn portion was inadequate. Not only the cord, but also the cotton tape itself was coloured, a much paler colour than the external surface. However, a perfectly even dyeing internally and externally was achieved by the following procedure:

A length of the tape was wound on to a spring cheese-holder to obtain a cheese of 700 g. in weight, and the package was fitted into a laboratory package-dyeing machine unit and, after scouring and an acid rinse, dyed in 7 kg. of a liquor containing:

Dye No. 1	4 g/l
Dye No. 2	3 g/l
Dye No. 3	1.5 g/l
Sodium nitrobenzene sulphonate	5 g/l
Common salt	100 g/l

The liquor was raised to 120°C during 20 minutes and maintained at 120—125°C for 30 minutes, then cooled to 90°C. Sodium carbonate was added in an amount to give 20 g/l and the liquor was circulated for a further 60 minutes at 90°C.

The material was then rinsed in cold water and hot water, scoured in a 0.1% solution of detergent for 15 minutes at the boil, rinsed again in hot and cold water, and finally drained and dried. Using:

Dye 1: the 1:2-chromium complex of the monoazo compound from cyanuric chloride, 4 - nitro - 4′ - amino-stilbene - 2,2′ - disulphonic acid and 6 - amino - 2 - (*o* - carboxyphenylazo) - 1 - naphthol - 3 - sulphonic acid (equimolar proportions).

Dye 2: 2 - [4′ - (2″ - chloro - 4″ - amino - *s* - triazin - 6″ - ylamino)2′ - ureidophenylazo]naphthalene - 3,6,8 - trisulphonic acid.

Dye 3: the copper complex of 6 - (2′ - chloro - 4′ - amino - *s* - triazin - 6′ - yl) - N - methylamino - 2 - [4″ - (2‴,5‴ - disulphophenylazo) - 5″ - methyl - 2″ - hydroxyphenylazo] - 1 - naphthol - 3 - sulphonic acid.

a very dark brown dyeing was obtained.

The following table gives a list of further dyes which have been found suitable for use in the new process. Column I gives the Colour Index reference or commercial name where this does not appear in the Colour Index, and Column II the general type of cellulose-reactive group involved.

Colour Index Black 8	monochloro-*s*-triazine
Brown 2	monochloro-*s*-triazine
Brown 7	monochloro-*s*-triazine
Brown 9	monochloro-*s*-triazine
Brown 17	monochloro-*s*-triazine
Brown 19	2,3-dichloroquinoxaline
Blue 2	monochloro-*s*-triazine
Blue 3	β-chloroethylaminosulphonyl
Blue 5	monochloro-*s*-triazine
Blue 19	β-sulphatoethylsulphonyl
Blue 21	β-sulphatoethylsulphonyl
Blue 25	β-chloroethylaminosulphonyl
Blue 26	monochloro-*s*-triazine
Blue 40	monochloro-*s*-triazine
Blue 46	monochloro-*s*-triazine
Blue 49	monochloro-*s*-triazine
Blue 53	3,6-dichloropyridazin-4-ylcarbonylamino
Blue 64	monochloro-*s*-triazine
Blue 71	monochloro-*s*-triazine
Green 5	monochloro-*s*-triazine
Green 8	monochloro-*s*-triazine
Orange 2	monochloro-*s*-triazine
Orange 7	β-sulphatoethylsulphonyl
Orange 12	monochloro-*s*-triazine
Orange 13	monochloro-*s*-triazine
Orange 23	β-sulphatoethylsulphonylamino
Orange 25	acryloylamide
Orange 32	β-phenylsulphonylpropionylamino
Orange 35	monochloro-*s*-triazine
Orange 43	5-chloro-6-methyl-2-methylsulphonyl pyramid-4-ylamino
Red 3	monochloro-*s*-triazine
Red 9	monochloro-*s*-triazine
Red 13	monochloro-*s*-triazine
Red 56	trichloropyrimidine
Red 58	monochloro-*s*-triazine
Yellow 3	monochloro-*s*-triazine
Yellow 6	monochloro-*s*-triazine
Yellow 15	β-sulphatoethylsulphonyl
Yellow 18	monochloro-*s*-triazine
Yellow 33	β-(4,5-dichloropyridaz-6-on-1-yl) propionyl
Reatex Brilliant Yellow 4RL	2-chlorobenzthiazol-6-ylcarbonylamino
Elisiane Brilliant Red B	1,4-dichlorophthalazin-6-yl-carbonylamino.

WHAT WE CLAIM IS:—

1. A process for dyeing cellulose textile materials in a tightly woven or densely packed form which renders them difficult to dye in level shades, which comprises contacting the material in an aqueous medium at pH 6—7 containing an electrolyte with a water-soluble reactive dyestuff at a temperature above 100°C until the desired penetration and exhaustion are achieved and thereafter fixing the dyestuff on the material by treatment of the coloured material with an acid-binding agent, the dyestuff being chosen in conformity with the test defined in the foregoing specification.

2. A process as claimed in claim 1 wherein the dyestuff used contains, as the reactive group, a monochloro-*s*-triazine group containing an amino, etherified hydroxy, anilino or substituted anilino group.

3. A process as claimed in claim 1 substantially as described in Example 1.

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